IV.F.8 Catalysts for Autothermal Reforming

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Objectives

- Develop advanced fuel processing catalysts that meet DOE performance requirements.
- Improve understanding of reforming reaction mechanisms, catalyst deactivation, and sulfur poisoning.
- Define operating parameters [e.g., O_2:C and H_2O:C ratios, temperature, gas-hourly space velocity (GHSV), and catalyst structure] to optimize catalyst performance and lifetime.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- I. Fuel Processor Startup/Transient Operation
- J. Durability
- M. Fuel Processor System Integration and Efficiency

Approach

- Building on our past experience, we are investigating two classes of materials, transition metal(s) supported on oxide substrates and perovskites.
- Determine catalyst performance (H_2 yield, CO_x selectivity, hydrocarbon breakthrough, fuel conversion) and stability as a function of catalyst composition, fuel composition and sulfur content, and operating parameters: O_2:C and H_2O:C ratios, temperature, GHSV.
- Conduct catalyst characterization and mechanistic studies to identify factors influencing activity and selectivity, causes of deactivation, and how sulfur affects catalyst activity.

Accomplishments

- Demonstrated that higher H_2 yields and lower hydrocarbon breakthroughs are achieved with Rh/alumina than with Rh/ceria for autothermal reforming (ATR) of gasoline.
- Developed a rapid aging process (24 h) that allows us to simulate changes that occur in the morphology of ATR catalysts during "hundreds or thousands of hours of operation."
- Determined that metallic Ni particles are formed on the surface of Ni-containing perovskites during ATR and that these particles may be necessary for ATR to occur.

Future Directions

- Improve catalyst durability and minimize deactivation by conducting characterization studies of catalysts before and after ATR to further our understanding of deactivation mechanisms.

- Improve sulfur tolerance of catalysts by increasing our understanding of sulfur poisoning mechanisms.

- Conduct mechanistic studies to increase our understanding of reaction pathways.

Introduction

On-board fuel processing of gasoline or other fuels to generate H_2 for automotive fuel cell systems presents many challenges: the fuels are complex mixtures consisting of both aliphatic and aromatic compounds, which reform at different rates and have differing propensities to form coke; fuels contain heteroatoms, such as sulfur, which can poison reforming catalysts; and fuels may contain additives, such as detergents, which can affect catalyst performance. Autothermal reforming (ATR), which combines partial oxidation and steam reforming, has been widely accepted as the most promising route for reforming these complex fuels to meet the efficiency, weight and volume, durability, and cost goals for on-board fuel processors. Because of the demanding conditions (e.g., high temperatures, high steam partial pressure, both oxidizing and reducing atmospheres) present in an ATR reformer, new catalysts are needed that are more active, more stable towards deactivation, and more resistant to both coke formation and sulfur poisoning than the existing Ni-based or other commercial catalysts currently used to produce H_2 by the steam reforming of natural gas.

We are investigating two different types of materials, oxide-supported transition metals and perovskites, as new ATR catalysts. Most of our work is focused on Group VIII metals (e.g., Rh, Ru, Pt, Pd, or Ni), either singly or in combination, supported on oxide substrates (such as alumina or ceria). In addition to investigating the role of the transition metal in catalyst performance, we are also examining the role of the metal-support interaction in determining the catalyst's performance, using techniques such as doping to form mixed-metal oxides to enhance the metal-support interaction to improve activity or stability. The oxide-supported transition metal catalysts have demonstrated near-equilibrium yields of H_2 from a number of fuels, including gasoline, diesel, and natural gas, exhibiting high catalytic activity and resistance to coking. We are investigating mixed non-noble metal oxides with the ABO_3 stoichiometry and the perovskite structure as an alternative to the oxide-supported transition metal catalysts because of concerns over the cost and, to a lesser extent, the supply of precious metals.

Approach

Catalysts are prepared as powders using the incipient wetness technique for oxide-supported transition metals and a glycine-nitrate combustion process for the perovskites. The catalysts are tested in a microreactor system using 0.1-2 g of powder for ATR of one or more of the following fuels: methane; isobutene; sulfur-free (<1 ppm) gasoline; a low-sulfur (nominally 30 ppm) gasoline; and a four-component mixture which is used as a surrogate for gasoline, referred to as benchmark fuel, consisting of isooctane (2,2,4-trimethylpentane), methylcyclohexane, xylenes, and 1-pentene, developed by Argonne National Laboratory (ANL). The sulfur-free and low-sulfur gasolines were purchased from Chevron-Phillips. The performance of each catalyst is screened over 8-24 h in a microreactor system where the H_2 yield, CO_x selectivity, and hydrocarbon breakthrough are determined as a function of operating parameters (O_2:C and H_2O:C ratios, reactor temperature, and GHSV), fuel composition and sulfur content. Catalysts exhibiting the highest H_2 yields and CO_x selectivities, and lowest hydrocarbon breakthroughs, are tested further for up to 100-1000 h to evaluate their stability. Selected catalyst compositions are then washcoated onto structured supports such as ceramic monoliths or metal foams. The washcoating was performed by Süd-Chemie, Inc. of Louisville, Kentucky. The structured supported catalysts are tested in a bench-scale 1-kW reactor system to investigate the effect of catalyst geometry on performance.

The catalyst samples are characterized before and after ATR to gain a better understanding of the relationship between the catalyst's morphology and chemical state and its performance. This understanding will help develop new formulations that are more active and more stable. Among the characterization techniques employed are N_2 adsorption, CO chemisorption, temperature-programmed reduction, X-ray absorption spectroscopy, neutron spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Results

Oxide-supported transition metal catalysts

Of the various transition metals that we have investigated, catalysts containing rhodium exhibit the highest H_2 yields and the lowest hydrocarbon breakthrough for ATR of methane, isobutene, gasoline, or diesel fuel. For Rh, as well as the other metals, the choice of the oxide support plays a significant role in determining the catalyst's performance. As shown in Figure 1, alumina supported Rh (Rh/alumina) exhibits a higher H_2 yield and lower hydrocarbon breakthrough (expressed as CH_4 equivalent) than ceria-supported Rh (Rh/ceria) for ATR of sulfur-free gasoline. X-ray absorption studies showed that the predominant Rh species were oxidized Rh before ATR and metallic Rh after ATR on both Rh/alumina and Rh/ceria. One possible explanation for the better performance of Rh/alumina is the ability of alumina to maintain a higher dispersion of Rh under ATR conditions compared to Rh/ceria. Rh dispersions of 81% and 31% were measured on Rh/alumina before and after being subjected to an aging process, which involved heating the catalyst for 24 h in a mixture of 33% H_2, 17% H_2O and 50% He at 900°C to simulate ATR conditions. (Assuming that there are a large number of Rh metal particles on the oxide surface, the term "dispersion" refers to the ratio of the total number of Rh atoms on the surface of these particles to the total number of Rh atoms). For Rh/ceria, Rh dispersions of 21% and 1% were measured before and after aging. A TEM study of the Rh/ceria before and after ATR showed a significant increase in the average grain size of the ceria particles and the loss of the sharp interface between the metal and the ceria
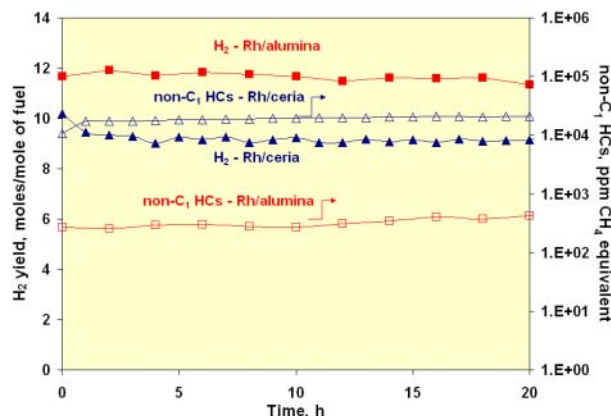

Figure 1. H_2 Yields and Hydrocarbon Breakthroughs for ATR of Sulfur-Free Gasoline Catalyzed by Rh/Alumina and Rh/Ceria

support, suggesting that ceria may be "encapsulating" the Rh, leading to a loss of available Rh on the surface. The higher dispersion of Rh on alumina is significant because the reaction rates exhibited by many oxide-supported metal catalysts are roughly proportional to the surface area, i.e., dispersion, of the supported metal.

Sulfur at the parts per million (ppm) level is known to poison many catalysts, leading to lower activity and poorer selectivity, by adsorbing on the catalyst's surface and blocking active sites where the reaction(s) occur. For ATR, sulfur tends to inhibit the reforming reactions, i.e., reactions involving oxygen or water to produce H_2 and CO/CO_2, to a greater extent than the C-C and C-H bond-breaking reactions, leading to coke formation on the catalyst surface and resulting in loss of activity. New Environmental Protection Agency (EPA) regulations will set the average sulfur content of gasoline sold in the U.S. at 30 ppmw (ppm by weight), with a maximum content of 80 ppmw S by 2006. Tests show that Rh catalysts are poisoned by 34 ppmw S in gasoline but that the loss in performance can be decreased by increasing the reaction temperature, as shown in Figure 2. The loss in performance is somewhat reversible, with an increase in H_2 production if the sulfur of the gasoline is reduced, as shown in Figure 3. In petroleum refining, it is known that the sulfur tolerance of Pt-based reforming catalysts can be improved when the Pt is alloyed with Pd.[1] We are investigating this approach, as well as other approaches such as adding a "sulfur getter" to
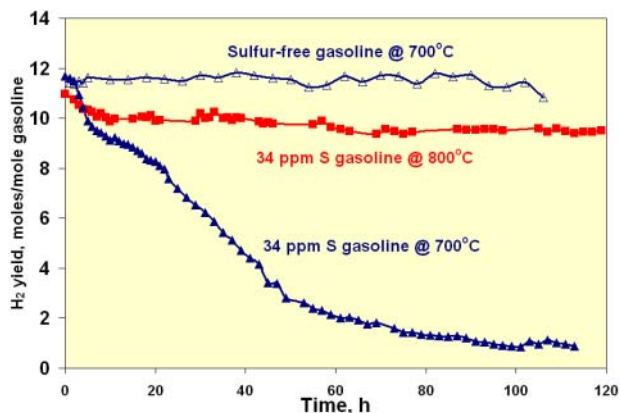
Figure 2. Effect of Temperature on the Yield of H_2 for ATR of 34 ppm Sulfur Gasoline Catalyzed by Rh/Alumina
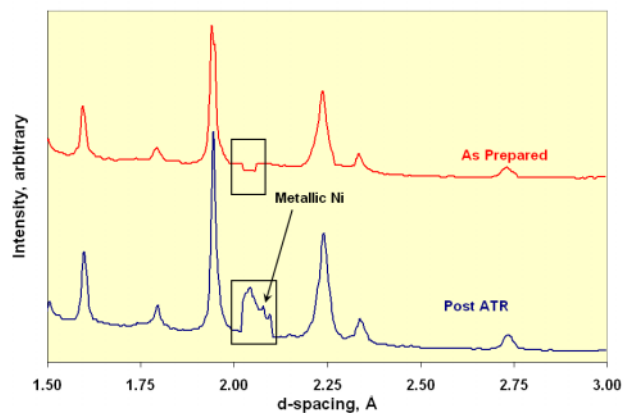

Figure 4. Neutron Spectra of $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ Before and After ATR Showing the Presence of Metallic Ni After ATR
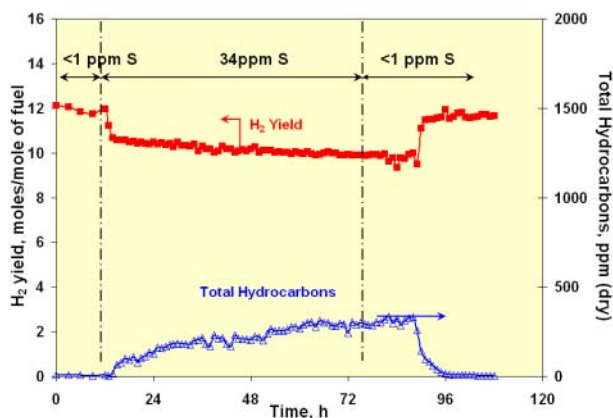

Figure 3. Effect of Sulfur Content of Gasoline on H_2 Yield and Hydrocarbon Breakthrough for ATR of Gasoline Catalyzed by Rh/Alumina
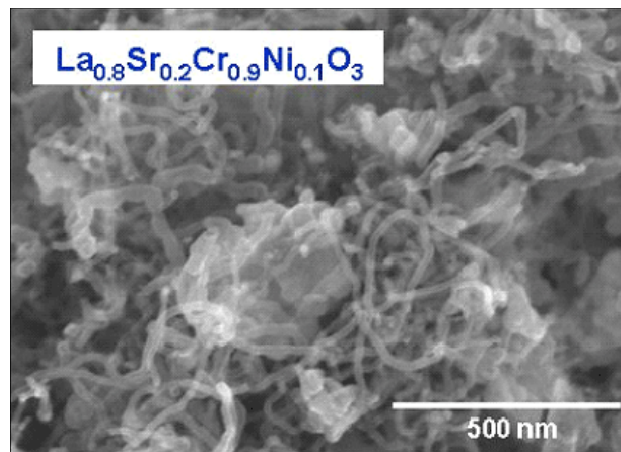

Figure 5. SEM Showing That Carbon Whiskers Are Formed on $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ During ATR

selectively adsorb the S, to improve the sulfur tolerance of the catalysts.

Perovskites

We have shown that the best perovskites for catalyzing ATR are based on A- and B-site-doped $LaNiO_3$.[2] However, the H_2 yield exhibited by doped $LaNiO_3$ is significantly lower than that observed with the Rh catalysts for ATR of gasoline under similar reaction conditions. For example, an initial yield of ~8 moles of H_2 per mole of gasoline is observed with $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$, compared to the ~12 moles observed with Rh/alumina. Furthermore, $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ suffers a greater

loss in activity with time on stream than is observed with the Rh-alumina catalyst. Neutron spectroscopy suggests that under the reducing environment of ATR, the perovskite undergoes a partial decomposition leading to the formation of small metallic Ni particles, as shown in Figure 4. It appears that these Ni particles may be required for the C-C and C-H bond-breaking reactions to occur. Carbon "whiskers" were observed on the surface of the catalyst by SEM as shown in Figure 5, similar to the carbon formation found on the surface of commercial Ni-alumina catalysts used for steam reforming natural gas.[3]

Conclusions

- Rh/alumina exhibits a higher H_2 yield and a lower hydrocarbon breakthrough than Rh/ceria for ATR of gasoline. The better performance of Rh/alumina is attributed to the ability of alumina to maintain a higher Rh dispersion than ceria.

- Rh catalysts are poisoned by sulfur in gasoline, although the poisoning effect of sulfur (reducing the H_2 yield and increasing the hydrocarbon breakthrough) can be reduced by increasing the reaction temperature.

- Our most active perovskite, $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$, is less active than the oxide-supported Rh catalysts for ATR of gasoline. Under ATR conditions, $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ decomposes to generate metallic Ni, which is believed to be necessary for the ATR to occur.

References

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2. Jennifer Mawdsley, Magali Ferrandon, Cécile Rossignol, James Ralph, Laura Miller, John Kopasz, and Theodore Krause, "Catalysts for autothermal reforming," 2003 Annual Progress Report, U.S. DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program.

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FY 2004 Publications/Presentations

1. "Reforming Catalysts for On-Board Fuel Processing," T. Krause, M. Ferrandon, and C. Rossignol, Presented at the 226th National American Chemical Society Meeting, September 7-11, 2003, New York, NY.

2. "Role of Catalysis in Fuel Processing for Fuel Cell Systems," T. Krause, Presented at the 4th DOE National Laboratory Catalysis Conference, October 22-24, 2004, Oak Ridge, TN.

3. "Rh-based Catalysts for Autothermal Reforming of Liquid Fuels into Hydrogen," M. Ferrandon and T. Krause, Presented at the 4th DOE National Laboratory Catalysis Conference, October 22-24, 2004, Oak Ridge, TN.

4. "Study of Perovskites as Autothermal Reforming Catalysts," J. Mawdsley, M. Ferrandon, J. Ralph, and T. Krause, Presented at the 4th DOE National Laboratory Catalysis Conference, October 22-24, 2004, Oak Ridge, TN.

5. "Perovskite Catalysts For the Autothermal Reforming of Liquid Hydrocarbon Fuels," J. Mawdsley, T. Krause, J. Ralph, J. Critchfield, D.-J. Liu, L. Miller, H.-K Liao, J. Kopasz, S. Ahmed, Presented at the 2003 Fuel Cell Seminar, November 3-7, 2003, Miami Beach, FL.